APPLYING IONIC LIQUIDS TO RARE-EARTH SEPARATIONS

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Abstract

A way to improve the sustainability of solvent extraction is to replace the organic diluents used in current separation processes by ionic liquids. The desirable properties of ionic liquids include a very low vapour pressure, which avoids air pollution and reduces the risk of fire. In order to successfully apply ionic liquid systems to rare-earth separation processes these systems need to be economic, simple and give high separation factors. For this purpose, undiluted ionic liquids with quaternary ammonium and phosphonium cations with nitrate anions have been investigated for the extraction of rare earths from aqueous nitrate solutions using EDTA as an aqueous complexant. At higher rare-earth concentration levels, the distribution ratios are loading-dependent making the extraction dependent on the composition of rare earths. Therefore the composition was modelled on the European deposit of Norra Kärr (Sweden).

Introduction

The use of ionic liquids for the separation of mixtures of rare earths through solvent extraction is a developing field with high potential because of both the intrinsically beneficial properties of ionic liquids and the suitable extraction properties of some ionic liquids.[1-3] Ionic liquids are per definition solvents consisting solely of ions and are typically made up of salts with organic components and are liquid at useful temperatures. The properties of ionic liquids generally include a very low vapour pressure. This can make incorporating them into solvent extraction processes a part of the transition towards greener processes since this reduces flammability and air pollution.[1] Ionic liquids can however only be considered green provided that they have a low persistency and a low toxicity. A part of this is the avoiding the use of fluorinated ionic liquids, due to their persistence in nature.[4]

Two reasonable starting points when using undiluted hydrophobic ionic liquids, without functional groups specific to rare-earth extraction, are choosing a suitable counter-ion that will create extractable complexes with the rare earths to be extracted and choosing an ionic liquid with properties suitable for solvent extraction. For the counter-ions, the most obvious choices are sulphate, chloride or nitrate, since the corresponding acids (H_2SO_4, HNO_3, HCl) can be used to dissolve rare-earth-containing starting materials. Sulphuric acid is somewhat unsuitable due to the low solubility of some rare-earth sulphate salts in solutions with high sulphate concentrations. Hydrochloric acid is a potential choice since rare-earth chloride complexes can be extracted using chloride ionic liquids, though only at very high chloride concentrations,

although suitable solvating extractant extractants can be used to extract from chloride systems.[6-8] The chloride-chloride (chloride in both phases) ionic liquid systems, such as tricaprylmethylammonium chloride for extraction of rare earths from chloride aqueous solutions, are unsuitable due to low distribution ratios.

Nitrates have historically been used for rare-earth separation systems since nitrates form highly extractable complexes with rare-earth ions. The use of tricaprylmethylammonium nitrate in rare-earth separation has strong precedents in the literature, with a number of investigations and patents, but these extractants are usually used diluted in molecular diluents and not as pure ionic liquids.[9–17] Two commercially available non-fluorinated hydrophobic ionic liquids suitable for solvent extraction were therefore chosen for this study: tricaprylmethylammonium chloride (Aliquat 336) and trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), both of which can have their chloride anions easily replaced by nitrate ions. These ionic liquids can also be used as diluents for other ionic liquids or classical extractants due to their physical properties, including a comparatively (to other ionic liquids) low viscosity when equilibrated with a water phase.

Gaudernack *et al.* described the use of quaternary ammonium nitrate dissolved in organic diluents to extract light rare earths from an aqueous nitrate solution, followed by extraction of the heavy rare earths using a quaternary ammonium thiocyanate dissolved in organic solvents for the primary purpose of separation yttrium from the other rare earths.[16] This process has an optimum at a nitrate concentration in the range of 5–7 M, with 0.5 M or less of rare-earth metals, using a nitrate salt (e.g. sodium or ammonium nitrate). The given acidity is stated as a range of pH values between 0.5 and 5, where extractability is higher at higher pH and separation increased at lower pH. Modification of the separation factors by aqueous complexants such as diethylene triamine pentaacetic acid (DTPA), followed by stripping by ammonium chloride and subsequent precipitation by oxalic acid when using quaternary ammonium nitrates dissolved in organic diluents to selectively extract lighter lanthanides was described by Bauer *et al.*[12]. Trimble et al. described the use of an amine extractant to extract light lanthanide followed by an acidic extractant extraction to remove heavy lanthanides, with the purpose of attaining pure yttrium by stripping it using an acidic scrub.[17] Morais *et al.* investigated the use of tricaprylmethylammonium nitrate dissolved in kerosene to separate gadolinium and europium in a sodium nitrate matrix with a separation factor of 2.0 that was independent of the nitrate concentration.[10] Lu *et al.* investigated the separation of praseodymium from neodymium using 0.6 M tricaprylmethylammonium nitrate in an aromatic diluent with DTPA used as an aqueous complexant.[11]

In this paper, we report on the separation of rare earths by extraction with tricaprylmethylammonium nitrate or trihexyl(tetradecyl)phosphonium nitrate from an aqueous nitrate feed solution containing EDTA as complexant. The significant progress, compared to some previous studies, proposed in this work is to proceed towards greener processes for the separation of rare earths. This is achieved by use of

nitrate ionic liquids in their pure form instead of diluted in, for example, kerosene in order to gain the benefit of ionic liquids and thereby having an insignificant vapour pressure. The fact that the concentration of the extractant is very high since the ionic liquid phase acts itself as the extractant also gives high distribution ratios. The growth in the number of products utilising rare-earth metals in their construction has led to a supply risk of rare earths which in turn has lead to the desire to develop geographically diverse resources of rare earths.[18] This study therefore uses a European rare-earth source as a model for the distribution of the aqueous solutions used for extraction studies.

The aqueous complexing agent ethylenediaminetetraacetic acid (EDTA) was used to increase separation factors. EDTA was chosen because of its favourable properties since it forms more stable complexes with heavy rare earths than with light rare earths. This increases the separation factors, since the extractant is a quaternary ammonium or phosphonium salt that extracts light rare earths preferentially.

Experimental

Tricaprylmethylammonium chloride (Aliquat 336) is a mixed quaternary ammonium salt containing mainly trioctylmethylammonium and tridecylmethylammonium chloride (Sigma-Aldrich, 88.2-90.6%). Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) is a phosphonium-based ionic liquid (Cytec Industries, 97.7%). To prepare the nitrate form of the ionic liquids, they were pre-equilibrated three times for 1 hour or more with a 2.5 M KNO_3 solution to exchange the chloride ions by nitrate ions. After three equilibrations, the chloride levels in the ionic liquid phase were under the instrumental detection limits (TXRF).

Hydrated rare-earth nitrate salts were obtained from Aldrich (Y 99.9%, Tb 99.9%, Sm 99.9%), Alfa Aesar (La 99.99%, Nd 99.9%, Dy 99.9%, Ho 99.9%, Yb 99.9%), Chempur (Pr, 99.9%) and Acros (Gd 99.9%). The following rare earth oxides were used: yttrium(III) oxide (Rhodia,99.99%), lanthanum(III) oxide (Aldrich, 99.99%), praseodymium(III,IV) oxide (Janssen chemicals, 99.9%), neodymium(III) oxide (Rhodia, 99.9%), samarium(III) oxide (Rare Earth Products Ltd, 99.9%), europium(III) oxide(Inframat Advanced Materials, 99.99%), gadolinium(III) oxide (Ventron LFA products, 99.9%), terbium(III,IV) oxide (Rare Earth Products Ltd, 99.99%), dysprosium(III) oxide (Rare Earth Products Ltd, 99.99%), holmium(III) oxide (Rare earth products Ltd, 99.99%), erbium(III) oxide (Acros Organics, 99.99%), thulium(III) oxide (GFS Chemicals, 99.9%), ytterbium(III) oxide (Rhodia, 99.9%), lutetium(III) oxide (Rare Earth Products Ltd, 99.9%). Ethylenediaminetetraacetic acid (Acros Organics, 99%) and potassium nitrate (Chem-lab, >99%). Sodium nitrate (Chem-Lab, >99%), ammonium nitrate (Chem-Lab, >99%). All dilutions were made using pure water (MilliQ, Millipore, >18 MΩ/cm). A Picofox S2 (Bruker) total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal content in solutions.

Batch solvent extraction experiments were performed using approximately 1 mL of each phase, unless other phase ratios were tested, in which case the ionic liquid

volume was increased. Samples were shaken at constant temperature (30 °C) using a TMS-200 turbo thermo shaker (Hangzhou Allsheng Instruments Co., Ltd) for 30 min, or longer when stated. The pH measurements were performed using a S220 SevenCompact pH/Ion meter (Mettler-Toledo) and a slimtrode electrode (Hamilton) and calibrated using pH 1.0 (Merck), 4.0 (Chem-Lab), 7.0 (VWR) and 10 (Fischer) buffers.

The distribution ratio (*D*) of a single metal is defined (equation 1) as the ratio of the total concentration in the ionic liquid phase ($[M]_{IL}$) by the total concentration in the aqueous phase ($[M]_{aq}$) after extraction and phase separation. The phase ratios are defined as the volume ionic liquid divided by the volume aqueous phase.

$$D = [M]_{IL} / [M]_{aq} \quad (1)$$

The basic assumption regarding the starting material was that an oxide concentrate has been formed from a starting ore material, thereby attaining an up-concentration and the possibility of choosing the chemistry of the separation process. The concentrate can in principle be in different forms such as oxide, carbonate, hydroxide, etc. The starting material for this work was based on a HREE-rich concentrates, such as the European deposit Norra Kärr in Sweden, with an average composition given in Table 1.[19] This initial process development, described in this paper, did not include the common impurities of the deposits ore body (zirconium, manganese, iron, etc.), It is also assumed that cerium is removed by a separate process step prior to (or in combination with) the re-dissolution of the oxide material. The optimal conditions for the separation process are dependent on the starting material and on the chosen concentrations for the re-dissolution of the oxide material.

High concentration nitrate aqueous phases with and without EDTA were prepared by dissolving in nitric acid a mixture of rare-earth oxides with a composition distribution mimicking that of the Norra Kärr deposit (Table 1, column A). A 6 M $NaNO_3$ matrix was spiked with a few representative rare-earth nitrate salts in order to study the nitrate extraction systems at low loading (Table 1, column B).

Table 1: Column A: composition of the concentrated rare-earth oxide solution in HNO_3. Columm B: concentrations of the solution spiked with rare earths for low concentration, high matrix experiments (6 M $NaNO_3$).

Metal	A (M)	B (M)
La	0.23	0.011
Pr	0.08	0.012
Nd	0.23	0.012
Sm	0.012	
Eu	0.002	

Gd	0.068	0.0081
Tb	0.02	0.0054
Dy	0.084	0.0071
Ho	0.02	0.0096
Er	0.029	
Tm	0.011	
Yb	0.045	0.015
Lu	0.011	
Y	1.3	0.0095

Results and Discussion

Extraction with nitrate-based ionic liquids

The distribution ratios in Table 2 indicate that, if the nitrate concentration is sufficiently high, nitrate pre-equilibrated Cyphos IL 101 is suitable for extracting all rare earths together. Tricaprylmethylammonium nitrate is better suited for group separations than trihexyl(tetradecyl)phosphonium nitrate since the separation factors between light rare earths (e.g. La, Pr, Nd) and heavy rare earths (e.g. Yb) and yttrium is greater for tricaprylmethylammonium nitrate. There is also a significant difference in the mid-range elements (Gd, Tb, Dy, Ho) that could be exploited to separate these elements.

Table 2: Distribution ratios in tricaprylmethylammonium nitrate (A) and trihexyl(tetradecyl)phosphonium nitrate (B) using an aqueous phase of 6 M $NaNO_3$ spiked with rare-earth nitrate salts. 30 min of mixing at 30 °C.

Metal	A	B
La	>300	430 ± 140
Pr	>250	230 ± 29
Nd	110 ± 13	200 ± 7.4
Gd	15 ± 1.0	74 ± 6.6
Tb	18 ± 1.2	120 ± 32
Dy	16 ± 1.6	86 ± 13
Ho	14 ± 1.5	72 ± 1.9
Yb	3.7 ± 0.7	18 ± 0.8
Y	4.7 ± 0.8	22 ± 1.1

However, the distribution ratios of ytterbium and yttrium are too high to be used for separations at the 6 M nitrate concentration. Therefore the distribution ratio was investigated as a function of the nitrate concentration between 3 M and 5 M nitrate by diluting the spiked 6 M sodium nitrate solution with pure water before contacting it with tricaprylmethylammonium nitrate (Figure 1). The separation factors remained constant over the range of nitrate concentrations while only the distribution ratios varied. The separation factors versus lanthanum for the heavy rare earths (Yb and Y)

are approximately 200 while for the medium rare earths (Gd, Tb, Dy and Ho) the separation factors vary between 50 and 70.

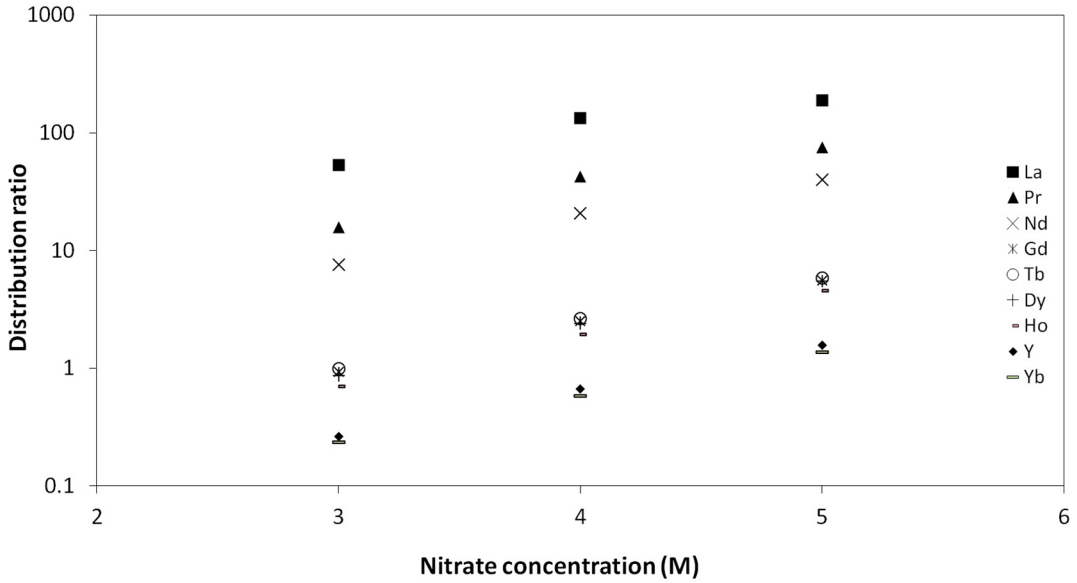

Figure 1: Distribution ratios for tricaprylmethylammonium nitrate versus concentration of sodium nitrate (3–5 M) at 1 h of mixing, 30 °C, pH approximately 2.

The separation factors coupled with the relevant distribution ratios are sufficient for a process to separate the light rare earths from the heavy and medium ones. However, there will be significant co-extraction of both medium and heavy rare earths. To increase the separation factors, an additional component is needed. An aqueous phase complexant can be used to increase the separation factors and reduce co-extraction. A suitable aqueous complexant is EDTA, which has a varying complex strength across the lanthanide series with stronger complexes for the heavier rare earths. This interacts well with the nitrated ionic liquid system since the light rare earths are to be extracted and the heavy remain in the aqueous phase, which is strengthened by complexing with EDTA. Additionally DTPA, citric acid, lactic acid and malonic acid were investigated, but were found to have undesirable properties at high loading, primarily precipitation or too low solubility of the acid.

A more acidic medium was tested as well (6 M nitric acid), but only very poor rare-earth extraction was observed ($D < 0.1$). Acidic and non-acidified chloride systems were investigated in Cyphos IL 101 and Aliquat 336, using 4 M sodium chloride and 8 M hydrochloric acid; however, only poor ($D < 0.1$) or no extraction at all was observed.

Aqueous complexant assisted separation with tricaprylmethylammonium nitrate

To evaluate the influence of pH on a system with the aqueous complexant EDTA, the pH of a highly loaded system with a high EDTA concentration was varied between 1.5 and 3.75 (Figure 2). The distribution ratios were lower at low pH. This shows that the pH has an impact on the distribution ratios; however, the separation factors remain fairly constant, as shown in Figure 3. This means that the following investigations into

the effect of lanthanide metal loading and EDTA concentration should have the same pH but that small variations will have only a small effect on separation factors.

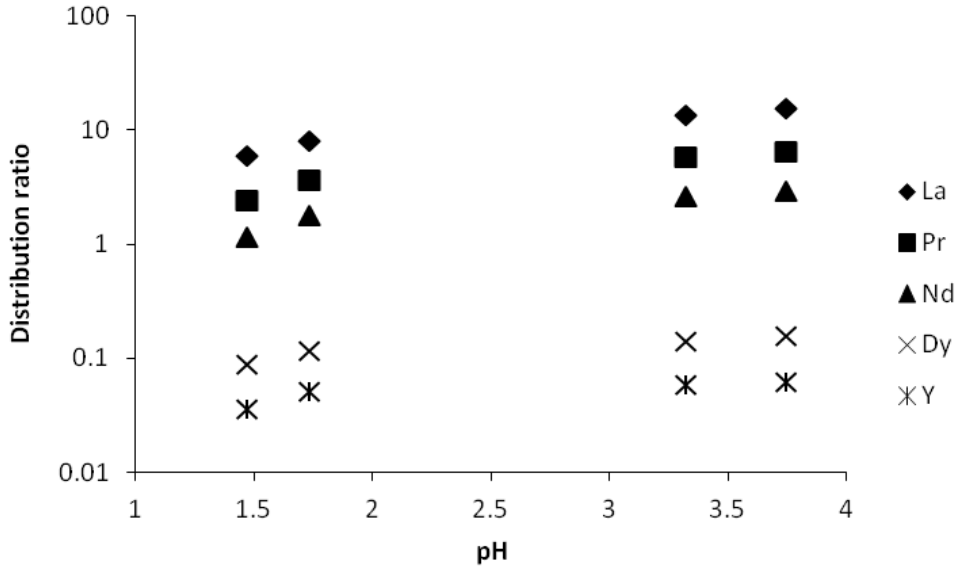

Figure 2: Distribution ratios at high metal concentrations (1.9-2 M) and high EDTA concentrations (0.75-0.8M) for tricaprylmethylammonium nitrate. The variations are due to the pH modifications. The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

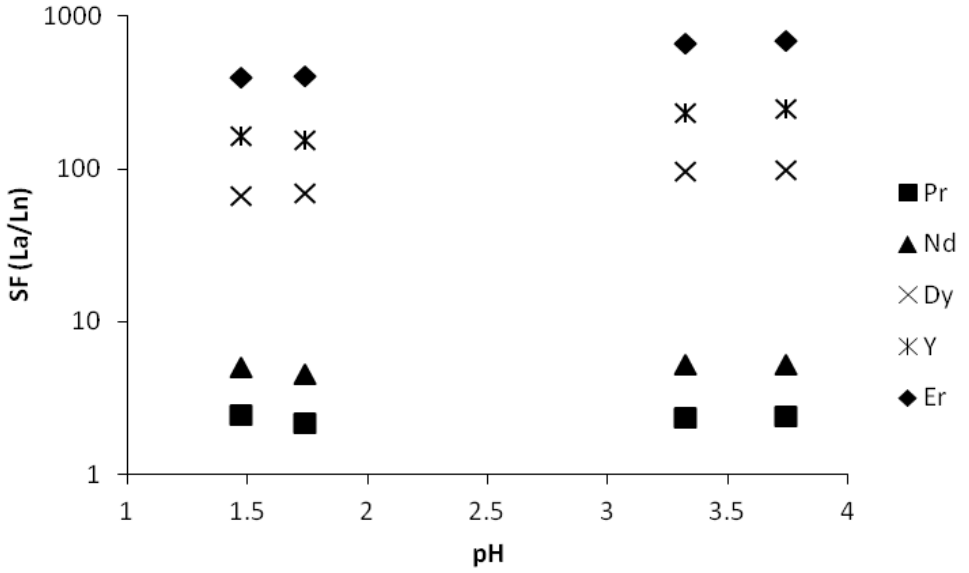

Figure 3: Separation factors at high loading (>93% of 2 M) and EDTA concentration (0.75-0.8M), the variation is due to 6M NH_3 additions to modify pH, in a 6 M nitrate matrix (ammonium nitrate). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

A high rare-earth metal loading (and thereby low additional added nitrate matrix) is desirable as is having as low an EDTA concentration as possible while maintaining a

high distribution ratio of elements to be extracted together with high separation factors. Increasing the EDTA concentration increases the binding strength of the aqueous phase for especially the heavy rare earths and this increases the separation factors, however, all distribution ratios are lowered too much at high EDTA concentrations. Based on the experiments with the 2 M mixed rare-earth solution (6 M nitrate), a series of dilutions down to 0.5 M of total metal content were investigated with varying EDTA concentrations utilizing an ammonium nitrate matrix to have a constant 6 M nitrate in the solutions. The pH in the solutions was kept at approximately pH 2. The effect of EDTA concentration on the 0.5 M rare-earth system is shown in Figures 4 and 5. The distribution ratios decrease strongly with the increasing EDTA concentration. All distribution ratios go below 1 already at 0.55 M EDTA. Up to 0.4 M EDTA the distribution ratio of lanthanum remains fairly high and the separation factors versus yttrium and heavy lanthanides such as dysprosium and beyond are approximately 10 000 or even higher.

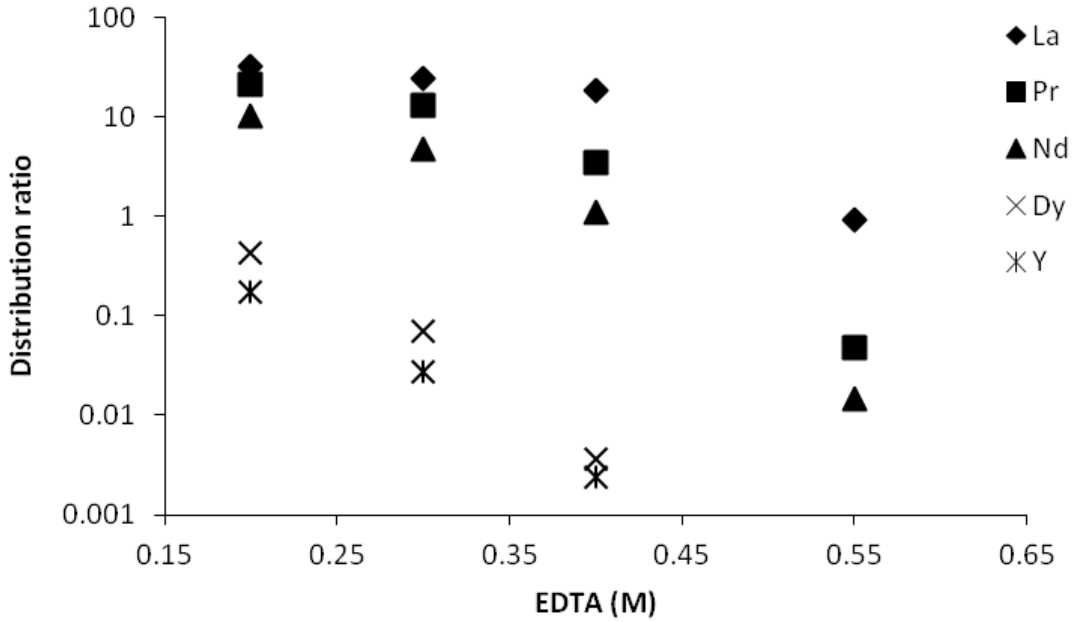

Figure 4: Distribution ratios at 0.5 M initial metal concentration in a 6 M nitrate matrix (4.5 M ammonium nitrate added). The composition of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

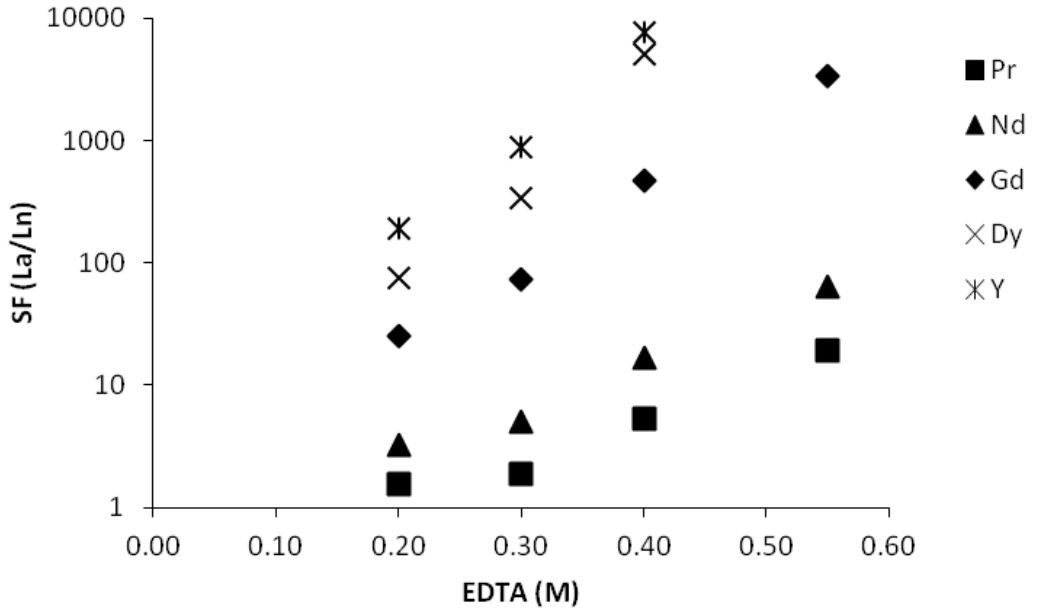

Figure 5: Separation factor versus lanthanum at 0.5 M initial metal concentration in a 6 M nitrate matrix (4.5 M ammonium nitrate added). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

The effect of EDTA concentration on a medium metal loaded system at 1 M rare-earth concentration is shown in Figures 6 and 7. The system is similar to the 0.5 M system with the differences that the distribution ratios are lower and the reduction with increasing EDTA concentration is lower. The separation factors are also somewhat lower with the highest being with the highest tested EDTA concentration with separation factors versus lanthanum for heavy rare earths about a factor of 10 lower at 1000. The separation factors are very dependent on the variation of the rare-earth concentration at a constant, high, EDTA (0.8 M) concentration (Figure 8).

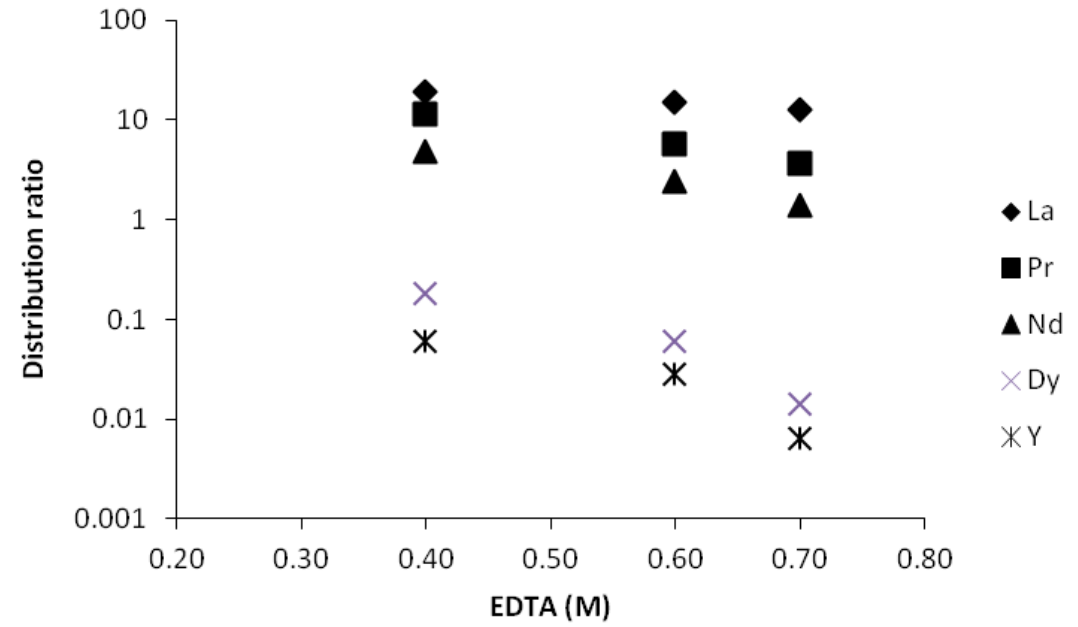

Figure 6: Distribution ratios at 1 M aqueous initial total metal loading in a 6 M nitrate matrix (3 M ammonium nitrate added). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

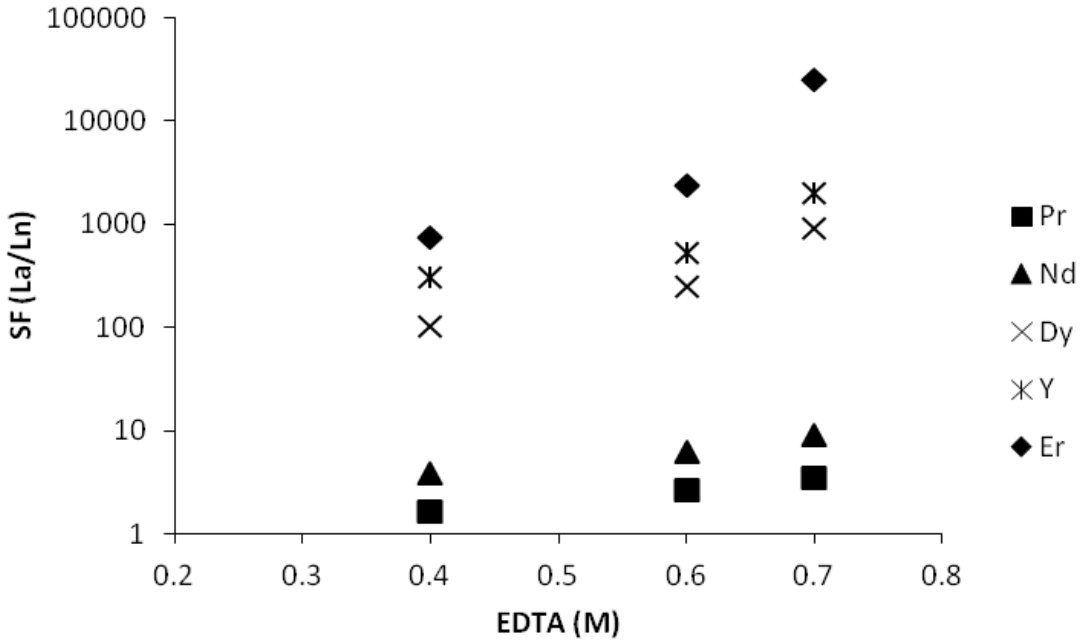

Figure 7: Separation factor versus lanthanum at 1 M initial metal loading in a 6 M nitrate matrix (3 M ammonium nitrate). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity. Separation factors versus EDTA concentration (M).

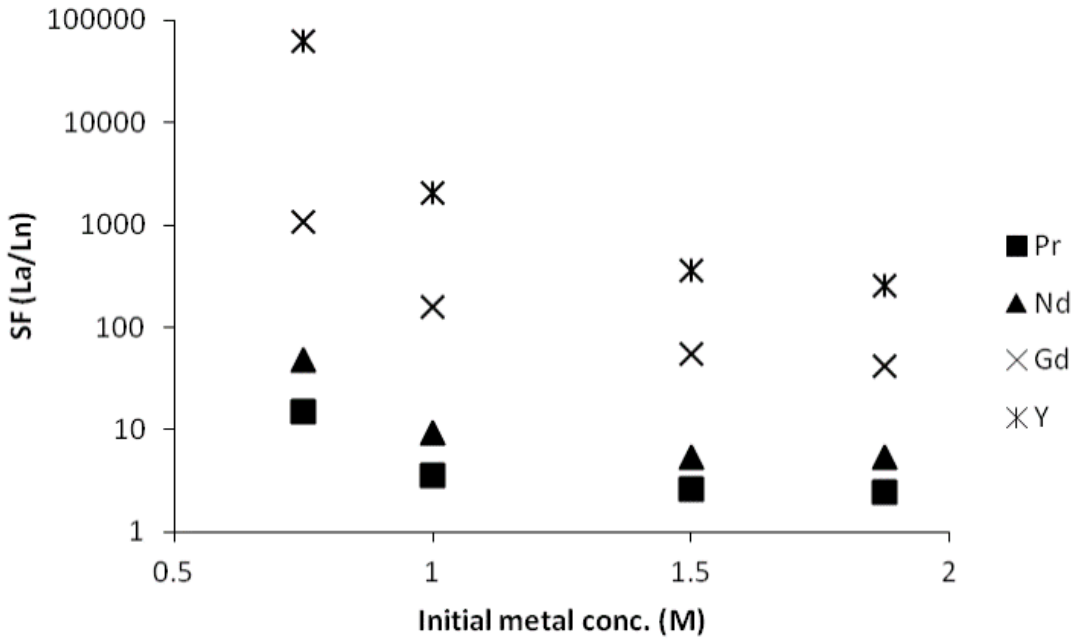

Figure 8: Separation factors versus total initial lanthanide concentration (M) with a constant EDTA concentration of 0.8 M, in a 6 M nitrate matrix (ammonium nitrate added). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

The rare-earth metal concentrations in the aqueous phase below 1 M at 0.8 M EDTA concentration have very high separation factors, but suffer from too low distribution ratios. The effect on the separation factors versus lanthanum is large, where the middle lanthanides have a separation factor of approximately 10000 at low initial metal concentration (0.75 M). However, the distribution ratio of neodymium has become somewhat too low since it will require many steps to completely extract the neodymium. Raising the nitrate concentration additionally can counteract this, for example, an ammonium nitrate matrix can be used to attain a nitrate concentration above 11 M without precipitation at room temperature.

The experimental results of using the desired high total nitrate concentration (11 M) with a reasonable initial total metal content (1 M after pH adjustments) combined with an EDTA concentration (0.2 M) optimized for an initial separation of material above dysprosium in the lanthanide series are shown in Table 3. Praseodymium and lutetium concentrations in aqueous (Pr) and organic (Lu) phase were below detection limits.

Table 3: Distribution ratios in tricaprylmethylammonium nitrate and using an aqueous phase of 11 M nitrate with a 1 M rare-earth initial metal concentration with a 0.2 M EDTA concentration. 2 h of mixing at 50 °C, phase ratio 2 (O:A).

Metal	Distribution ratio	Separation factor (La)
La	520	1
Pr	-	-
Nd	42	13
Sm	6.3	83
Eu	4.7	110
Gd	4.1	130
Tb	2.7	190
Dy	1.1	480
Ho	0.5	1100
Er	0.2	3500
Tm	0.01	35000
Yb	<0.01	82000
Lu	-	-
Y	0.4	1200

Conclusions

A system for liquid-liquid extraction based on the ionic liquid tricaprylmethylammonium nitrate, has been investigated for rare-earth separations in pure form using trace-level and high concentration of rare earth in nitrate aqueous solutions with and without EDTA. It was shown that high distribution ratios and separation factors can be achieved using this system and that the distribution ratio decreases with increasing atomic number across the lanthanide series. The separation factors were independent of the nitrate concentration and were improved by using EDTA as an aqueous phase complexant to increase the separation factor for the heavier rare earths. The system behaves favourably when the nitrate concentration is maximized due to the need to increase distribution ratios.

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References

1. *M. Dietz, "Ionic liquids as extraction solvents: Where do we stand?", Sep. Sci. Technol., 41 (10) 2047-2063 (2006).*
2. *Z. Kolarik, "Ionic Liquids: How Far Do they Extend the Potential of Solvent Extraction of f-Elements?", Solvent Extr. Ion Exch., **31** (1) 24-60 (2013).*
3. *Y. Liu, J. Chen and D. Li, "Application and Perspective of Ionic Liquids on Rare Earths Green Separation", Sep. Sci. Technol., **47** (2) 223-232 (2012).*
4. *S. Wellens, B. Thijs and K. Binnemans, "An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids", Green Chem., **14** (6) 1657-1665 (2012).*
5. *M. J. Earle and K. R. Seddon, "Ionic liquids, Green solvents for the future", Pure Appl. Chem., **72** (7) 1391-1398 (2000).*
6. *A. I. Mikhailichenko, E. G. Goryacheva, N. P. Sokolova, N. M. Aksenova, L. V. Vdovina and A. P. Emelyanov, "Extraction Of Rare-Earth Elements From Chloride Solutions By Salts Of Quaternary Ammonium Bases", Sov. Radiochem., **26** (1) 25-29 (1984).*
7. *P. K. Khopkar and J. N. Mathur, "Extraction Of Trivalent Actinides And Lanthanides By Tertiary And Quaternary Amines From Concentrated Chloride Solutions", J. Inorg. Nucl. Chem. **43** 1035-1040 (1981).*
8. *Kristian Larsson, Christian Ekberg and Arvid Ødegaard-Jensen, "Using Cyanex 923 for selective extraction in a high concentration chloride medium on nickel metal hydride battery waste", Hydrometallurgy, **129-130** 35-42 (2012).*
9. *M. Černá, E. Volaufová and V. Rod, "Extraction of light rare earth elements by amines at high inorganic nitrate concentration", Hydrometallurgy, **28** (1992).*
10. *C. A. Morais and V. S. Ciminelli, "Selection of solvent extraction reagent for the separation of europium(III) and gadolinium(III)", Miner. Eng., **20** 747–752 (2007).*
11. *D. Lu, J. Horng and Y. Hoh, "The separation of neodymium by quaternary amine from didymium nitrate solution", J. Less-Common Met., **149** 219–224 (1989).*
12. *D. J. Bauer and R. E. Lindstrom, "Differential extraction of rare-earth elements in quaternary ammonium compound-chelating agent systems", Bureau of Mines Report of Investigations 7524, (1971).*
13. *I. Komasawa, K. Hisada and M. Miyamura, "Extraction and separation of rare-earth elements by tri-n-octylmethylammonium nitrate", J. Chem. Eng. Jpn., **23** (1990).*
14. *J. Preston, Hydrometallurgy, "The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide", **42** 151–167 (1996).*
15. *D. J. Bauer and R. E. Lindstrom, "Selective extraction and separation of lanthanides with a quaternary ammonium compound", US patent, 3323857 (1967).*
16. *B. Gaudernack, G. Hannestad and I. Hundere, "Process for separation of yttrium from lanthanides", US patent, 3821352 (1974).*
17. *C. Trimble and D. Strott, "Yttrium purification process", US patent, 3640678 (1972).*
18. *European Commission, "Critical raw materials for the EU", Report of the Ad-hoc Working Group on defining critical raw materials, (2010).*
19. *G. C. Reed, "NI 43-101 Technical Report, Norra Kärr REE - Zirconium Deposit, Gränna, Sweden", Pincock, Allen & Holt, (2011)*